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Dr. Richard S. Miller

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Molecular Dynamics Simulation of Liquid Nitromethane Shocked to 143 Kbar

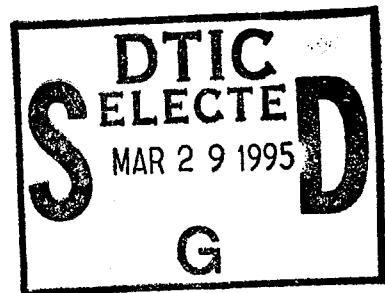
by

Jorge M. Seminario, Monica C. Concha and Peter Politzer

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Department of Chemistry
University of New Orleans
New Orleans, LA 70148

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<p>A molecular dynamics simulation, using a force field established by density functional calculations, has been used to investigate structural and vibrational frequency shifts that accompany a compression from 1 bar, 300 K to 143 kbar, 600 K. Under the latter conditions, most pairs of nitromethane molecules are found to be linked by two hydrogen bonds, instead of the one that is observed at 1 bar, 300 K. The computed shifts in the CN and NO₂ stretching frequencies are in good agreement with experimental results.</p>			
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Introduction

Greater insight into the response of an energetic material to a sudden increase in pressure would significantly enhance our understanding of detonation processes and our ability to design less sensitive compounds without sacrificing high performance levels. In this connection, there have been a number of investigations of the vibrational spectra of nitromethane, a prototypical energetic molecule, under both ambient conditions and also when shocked to higher pressures [1-10]. These studies, which sometimes produced conflicting results, have been briefly summarized by Pangilinan and Gupta [11], who have themselves carried out a detailed analysis of the vibrational behavior of liquid nitromethane when shocked to various pressures up to 144 kbar.

We have recently begun an extended density functional (DF)/molecular dynamics (MD) study of liquid nitromethane [12]. Our objective is to assess the feasibility of this approach for reproducing vibrational spectra and other experimental measurements; if successful, this would be a computational tool for predicting the properties of proposed energetic materials that have not yet been synthesized. In the first phase of this work [12], we simulated liquid nitromethane at ambient conditions (300 K and 1 bar). We will now increase the pressure to 143 kbar, and focus specifically upon the CN, NO₂ and CH₃ stretching frequencies. Our results will be compared to those obtained by Pangilinan and Gupta [11].

Procedure

We began with the system that we had created earlier [12]. This consisted of 216 nitromethane molecules at 300 K and a density of 1.139 g/cm³, in a cubic box with dimension 26.79 Å (chosen to reproduce the experimental density [13]). The intermolecular force field had been established by using a nonlocal density functional technique (Gaussian 92/DFT [14], Becke exchange [15] and Lee-Yang-Parr correlation [16] functionals, 6-31G** basis set) to compute the required molecular properties: optimized geometry, force constants and atomic charges. The charges were updated by another DF calculation during the course of the simulation.

In the present work, we again use the program CHARMM for the molecular dynamics simulations [17], with periodic boundary conditions, and the Verlet algorithm for the dynamics [18]. Since we now wish to reproduce a shocked state at 600 K and 143 kbar, the volume of the box was compressed to 55% of its original value (as calculated by Pangilinan and Gupta [11]). The number of nitromethane molecules was maintained at 216. The temperature was increased from 0 K to 300 K in increments of 10 K every 0.5 ps (1000 steps). At 300 K, the box was equilibrated for 5 ps and then heated to 600 K in increments of 50 K per 0.5 ps.

As was pointed out earlier [12] and will be seen again in this paper, the total pair correlation function g_{AB} for atom types A and B may not be very meaningful when there are two or more atoms of A and/or B in the molecule. For this reason we resolve g_{AB} into partial pair correlation

functions $g_{AB}^{(m)}$ which reflect separately the possible individual interactions between all A and B atoms in any two molecules [12]. For a system of N molecules, each having N_A atoms of type A and N_B of type B, the total pair correlation function g_{AB} can be defined by eq. (1):

$$g_{AB}(r) = \frac{V}{N_A N_B \frac{N(N-1)}{2}} \sum_{i=1}^N \sum_{j=i+1}^N \sum_{k=1}^{N_A} \sum_{l=1}^{N_B} \left\langle \delta\left(\vec{r} - \vec{r}_{A_i^k B_j^l}\right) + \delta\left(\vec{r} - \vec{r}_{A_j^k B_i^l}\right) \right\rangle \quad (1)$$

We define the partial pair correlation functions by eq. (2):

$$g_{AB}^{(m)}(r) = \frac{V}{\frac{1}{2}N(N-1)} \sum_{i=1}^N \sum_{j=i+1}^N \left\langle \delta\left(\vec{r} - \vec{r}_m^{ij}\right) \right\rangle \quad (2)$$

in which

$$\vec{r}_m^{ij} \in \left\{ \vec{r}_{A_i^k B_j^l} \right\} \cup \left\{ \vec{r}_{A_j^k B_i^l} \right\} \text{ such that } r_1^{ij} \leq r_2^{ij} \leq r_3^{ij} \leq \dots \leq r_{2N_A N_B}^{ij}$$

It follows that,

$$g_{AB}(r) = \frac{1}{2N_A N_B} \sum_{m=1}^{2N_A N_B} g_{AB}^{(m)}(r) \quad (3)$$

Finally, the CN, NO₂ and CH₃ stretching vibrational frequencies at both sets of conditions were calculated by means of the Fourier transforms of the autocorrelation functions of the respective bond variations during sample times of 10 ps (20,000 steps); this was done using routines that are available in CHARMM.

Results and Discussion

Figure 1 shows the partial pair correlation functions for the 12 possible O···H interactions between any two nitromethane molecules. The first two peaks, at about 2.0 Å and 2.6 Å, are both indicative of C–H···O hydrogen bonding [19,20]; thus, at 600 K and 143 kbar, a substantial number of pairs of nitromethane molecules are evidently linked through two hydrogen bonds. At 300 K and 1 bar, on the other hand, the first two peaks were about 2.3 Å and 3.2 Å [12]; this clearly indicates one hydrogen bond, but implies that there is usually not a second. In the lower portion of Figure 1 is the total OH pair correlation function, which is the average of the other twelve. This function conveys no useful information for liquid nitromethane, and can actually be misleading. At 300 K and 1 bar, it is essentially unstructured, and fails to reveal the hydrogen

bonding [12]; at 600 K and 143 kbar it does have several peaks, but only one that corresponds to hydrogen bonding.

Figures 2 and 3 present the partial pair correlation functions for the four possible C...O interactions, for both sets of conditions. These fully support our conclusions concerning hydrogen bonding in these systems. At the lower temperature and pressure there is one major peak, at the higher there are two; all are in the vicinity of 3.0 Å, which is fully consistent with C-H...O hydrogen bonding [19,20]. The total CO pair correlation function at 600 K and 143 kbar is again not able to show that there are two hydrogen bonding interactions.

In Figure 4 is shown the portion of the computed vibrational spectrum that corresponds to CN stretching, at both 300 K, 1 bar and 600 K, 143 kbar. The respective frequencies, 942.6 and 993.5 cm^{-1} , are in good agreement with the experimental values, 917 and approximately 969 cm^{-1} [11]; the computed and experimental frequency shifts are accordingly nearly identical.

For the NO_2 stretching vibration, we found the shift to be 30 cm^{-1} , compared to the measured value of about 42 cm^{-1} [11], with error bars of $\pm 10 \text{ cm}^{-1}$. The greatest magnitude of disagreement was in the shift in the CH_3 stretching frequency, for which we obtained 27 cm^{-1} while the experimental is approximately 85 cm^{-1} [11]. However the actual frequencies are relatively high, in the neighborhood of 3000 cm^{-1} , so that the discrepancies may only be 1% - 2%. Pangilinan and Gupta suggest that the unexpectedly large CH_3 shift may be due to intermolecular interactions involving the hydrogens. It may be, therefore, that we need to modify the intermolecular force field to reflect the fact that at 600 K, 143 kbar, most pairs of molecules are linked through two hydrogen bonds. The time step might also need to be changed.

Summary

We have used a combined density functional/molecular dynamics approach to study changes in the properties of liquid nitromethane when it is shocked from 300 K, 1 bar to 600 K, 143 kbar. There is definite evidence of hydrogen bonding under both sets of conditions; at the higher pressure, most pairs of molecules are linked through two hydrogen bonds. We are able to reproduce quite well the shifting of stretching vibration frequencies to higher values as the pressure increases.

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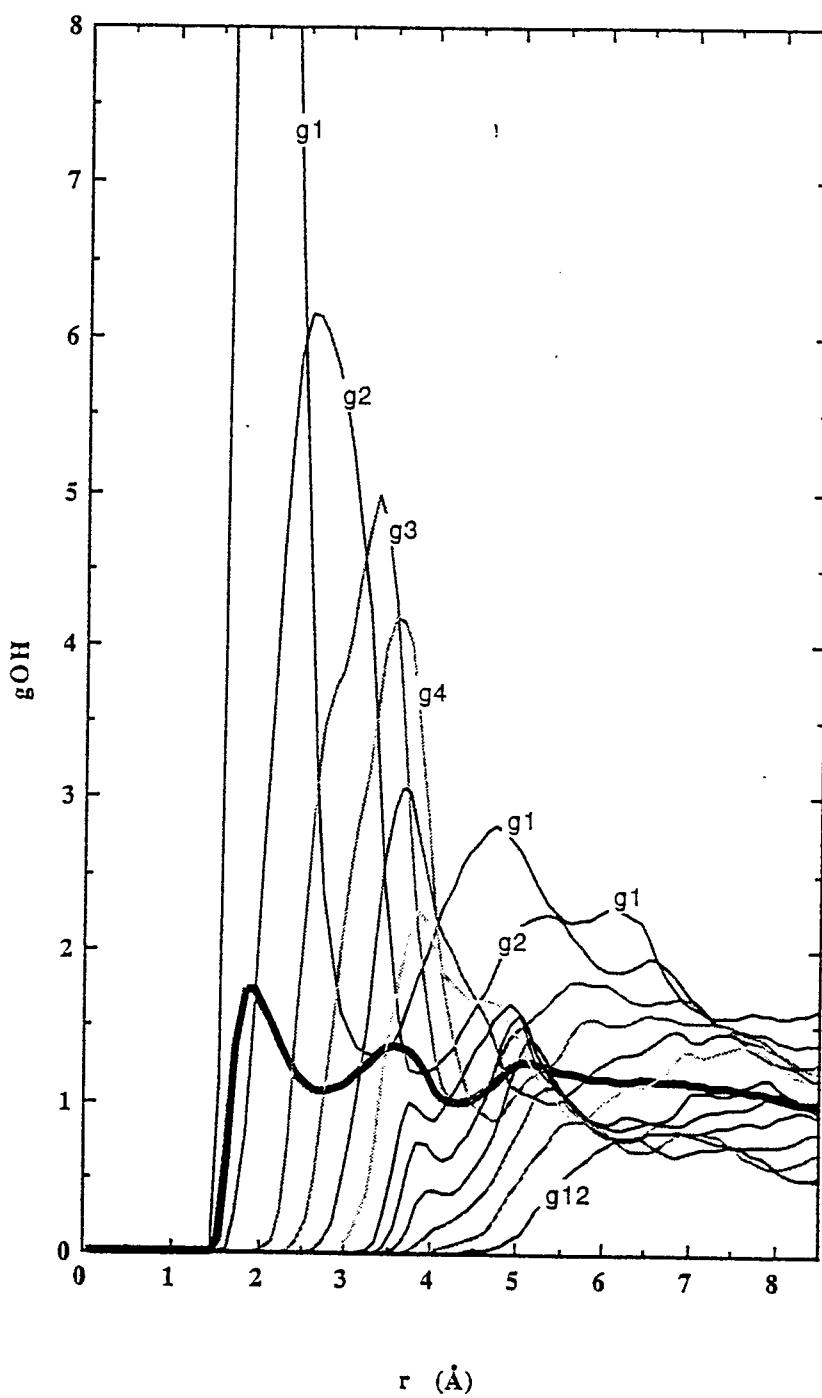


Figure 1. Calculated OH total (thick curve) and partial pair correlation functions for liquid nitromethane at 143 kbar and 600 K. The 12 partial pair correlation functions correspond to the possible O-H interactions between two nitromethane molecules.

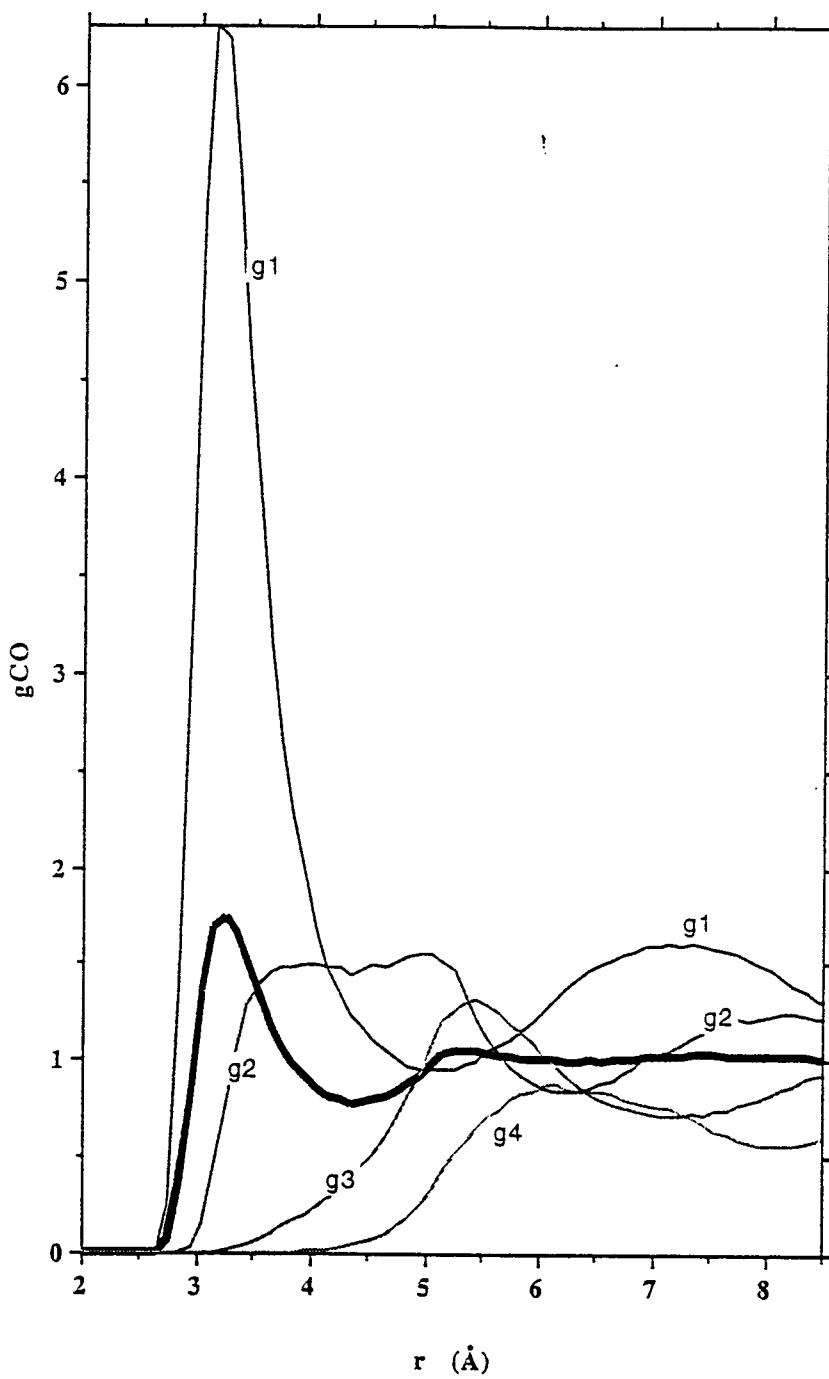


Figure 2. Calculated CO total (thick curve) and partial pair correlation functions for liquid nitromethane at 1 bar and 300 K. The four partial pair correlation functions correspond to the possible C---O interactions between two nitromethane molecules.

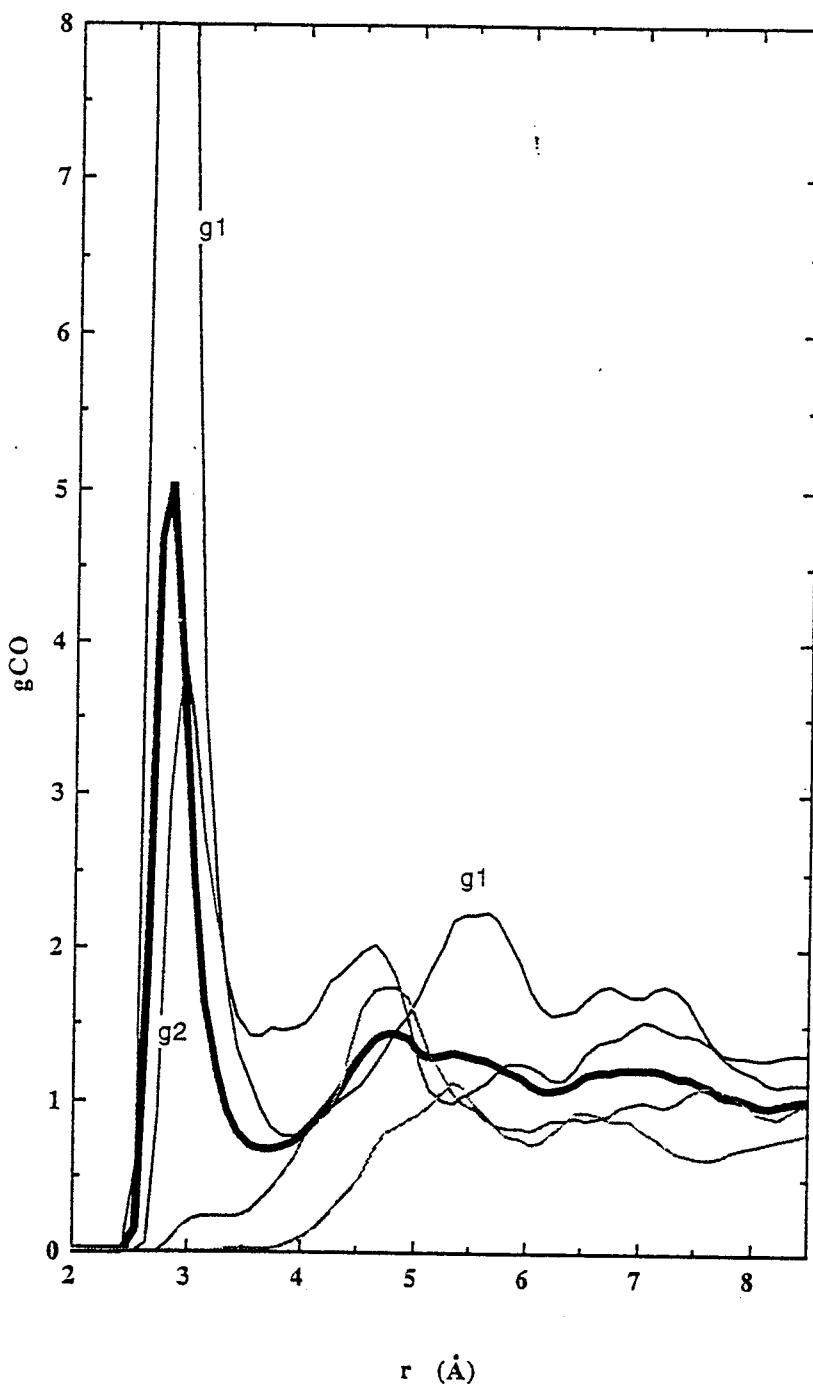


Figure 3. Calculated CO total (thick curve) and partial pair correlation functions for liquid nitromethane at 143 kbar and 600 K. The four partial pair correlation functions correspond to the possible C···O interactions between two nitromethane molecules.

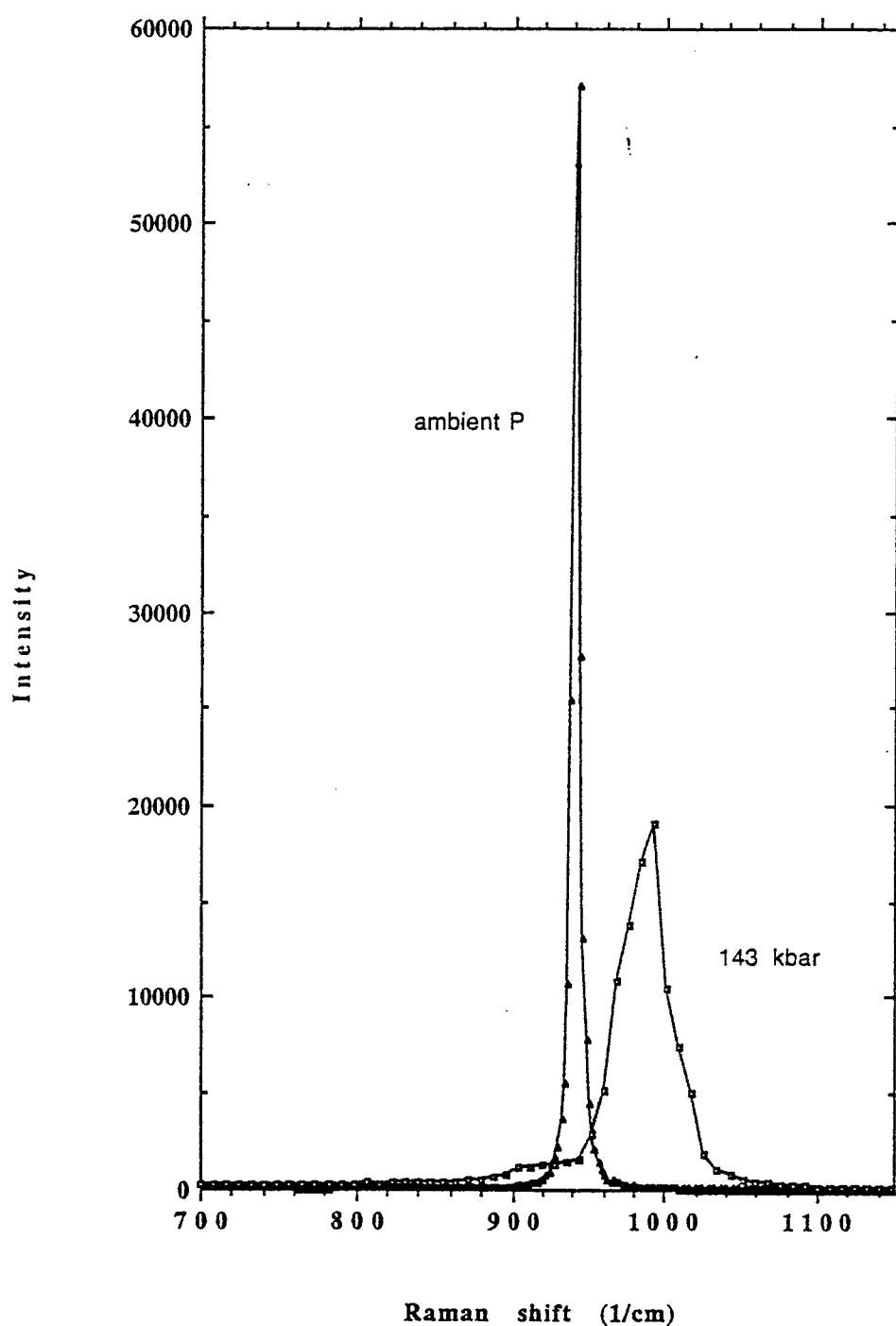


Figure 4. CN stretching vibration at ambient (1 bar) pressure and at 143 kbar.